SORPTION STUDIES ON SILICA XEROGEL.

A Thesis presented to University Sains Malaysia

for the degree of Master of Science in Chemistry.

by

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ABSTRAK

Penyerapan nitrogen pada suhu 77.4°K telah digunakan untuk mengkaji perubahan jalinan yang berlaku apabila xerogel silika perdagangan dikenakan proses penuaan melalui pencucian dan pemanasan yang berpanjangan semasa penceriaan silika dan dengan mendedahkannya ke atmosfera. Rupabentuk isotem-isotem yang didapati dari semua sampel xerogel yang dikaji itu menyerupai isotem-isotem yang digolongkan oleh Brunauer sebagai Jenis IV. Analisis taburan liang dan juga analisis yang menggunakan kaedah-t telah dilakukan pada semua isotem. Empat keluk-t standard telah digunakan dalam pembinaan plot-t dan didapati bahawa beberapa keluk-t standard itu lebih sesuai daripada yang lain. Dari analisis taburan liang didapati bahawa luar permukaan kumulatif tidak cocok dengan luas permukaan BET nitrogen dan isipadu liang itu tidak cocok dengan isipadu liang Gurvitsch bagi dua sampel itu sahaja. Tetapi sampel-sampel lain menunjukkan persesuaian yang lebih baik. Dengan bantuan keluk pengiaman berserta keputusan analisis taburan liang dan plot-t, rupabentuk gel yang paling mungkin sekali dapat dijelaskan.

Kecekapan proses penceriaan di mana xerogel perdagangan dipanaskan dengan asid dan kemudian dicuci dengan air suling untuk mengasingkan bendasing-bendasing ion dari gel juga telah dikaji. Ternampak keputusannya menunjukkan bahawa memang agak senang untuk mengasingkan bendasing-bendasing ion yang ada di permukaan gel itu tetapi sangat susah untuk mengasingkan bendasing yang mungkin ada di dalam gel tersebut.

Pengkajian-pengkajian menunjukkan bahawa semasa gel taktulin mengalami proses penuaan samada dengan mendedahkannya ke atmosfera atau secara mencucinya dengan air suling pada suhu 30°C, taburan saiz menjadi lebih lebar dan jejari liang purata pun bertambah. Namun demikian, perubahan dalam jalinan xerogel apabila xerogel itu dibiarkan mengalami proses penuaan atmosfera dan pencucian itu nampaknya tidak sama. Xerogel yang diceriakan melalui pencucian dengan air suling, nampaknya, mengalami penuaan atmosfera yang kurang dari xerogel taktulin.

The studies show that when an impure xerogel is subjected to ageing either by exposure to the atmosphere or by washing in distilled water at 30 ^{o}C, the pore-size distribution becomes broader and the average pore radius increases. However, the changes in the texture of the xerogel when it is subjected to atmospheric ageing and washing appear to be different. It also seems that a xerogel which has already been washed and purified undergoes relatively less atmospheric ageing than an impure xerogel.

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CONTENTS

CHAPTER 1 INTRODUCTION

1-1 Aim

Ageing is said to occur in an active solid when there is a change in the substance as manifested by a decrease in specific surface energy. The process by which this is accomplished, usually involves one or more of the following; surface diffusion, bulk diffusion, recrystallisation, cementing together of adjacent particles. As a result of ageing, various textural changes occur. In the case of porous solids, these changes are characterised by particle size, porosity, specific surface area, specific pore volume etc.

The ageing phenomenon can be brought about by a variety of ways such as by immersion in aqueous solutions, by storage in the atmosphere, by exposure to steam and by heating the solid to high temperatures. In the application of active solids to industrial and other processes, one or more of the factors which can promote or accelerate ageing are invariably encountered. This present work was undertaken to investigate the ageing of a commercial silica xerogel by nitrogen adsorption. The following general procedures were adopted for the ageing study:-

(i) exposure of the xerogel to the atmosphere.

(ii) prolonged washing of the xerogel in distilled water.

The second procedure was selected because the usual method employed by previous workers [1-5] to remove ionic impurities from

commercial xerogels is by repeated washing with distilled water after treatment with mineral acids. As such, one of the main aims of this project was to study any ensuring textural changes in the xerogel during the purification. The method employed for the purification process was also examined to ascertain to what extent it was possible to remove the ionic impurities in the xerogel. For ageing under the first procedure, changes in the surface structure of an aged impure and an aged purified gel were compared to determine the influence of ionic impurities on atmospheric ageing and to see if there is any similarity between ageing by exposure to the atmosphere and by washing.

1-2 Structure of Silica Gel.

Electron micrographs have shown that silica gel comprises of an aggregate of roughly spherical elementary or discrete particles [6,7], the average particle size being 30 to 60 Å. Okkerse [8] has described the elementary particles as thus:- "An elementary particle consists of an irregular 3-D network of SiO_4 tetrahedron, each silicon atom being linked to 4 oxygen atoms and each oxygen being linked to 2 silicon atoms. At certain sites, the elementary particles may be linked together by Si-O-Si bridges. The particle surface is covered with OH groups which are responsible for the hydrophilic nature of normal silica".

The pore system within this aggregate is formed by the open spaces between the elementary particles (see Fig. 1-1). The

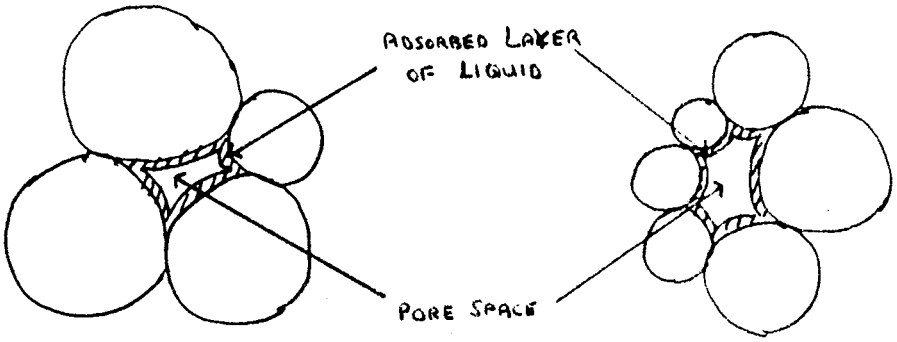

FIG.1-1 PORE STRUCTURE OF SILICA GEL

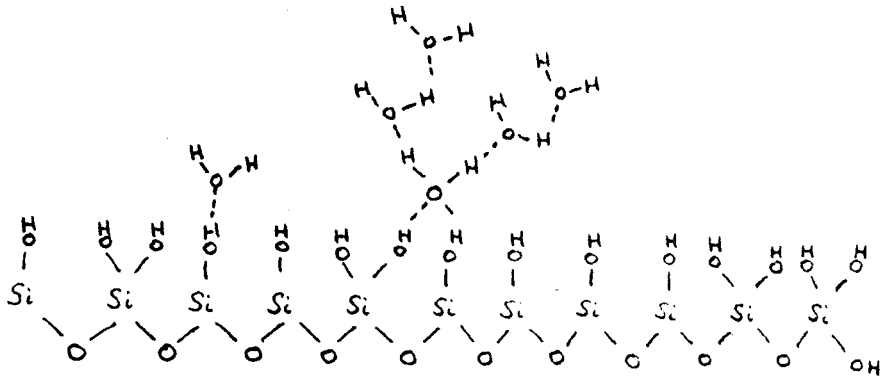

FIG.1-2 POSSIBLE ARRANGEMENTS OF THE OH-GROUPS ON THE SILICA SURFACE.[8]

porous texture of silica gel depends on the size and packing of the discrete particles. When the silica gel is heated at high temperatures (600 to 700 ^{o}C), they undergo sintering [9,10], and the pores collapse to give rise to a non-porous system.

1-3 Surface Structure Of Silica Gel.

In discussing the surface structure of the silica gel, it may perhaps be instructive to first consider the mode of formation of the silica hydrogel.

It is a well known fact that silicic acid can undergo polymerisation via the formation of siloxane bonds with the expulsion of water molecules according to the reaction scheme as shown below:-

$$(OH)_3SiOH + HOSi(OH)_3 \longrightarrow (OH)_3Si\text{-}O\text{-}Si(OH)_3 + H_2O$$

$$\downarrow Si(OH)_4$$

$$(OH)_3Si\text{-}O\text{-}Si(OH)_2 - Si(OH)_3 + H_2O$$

and so on.

Or in general,

$$(SiO_xH_y)_z - SiOH + OHSi\text{-}(SiO_aH_b)_c \longrightarrow (SiO_xH_y)_z - Si\text{-}O\text{-}Si\text{-}(SiO_aH_b)_c + H_2O$$

If the condensation reaction is allowed to carry on further, a polymeric colloidal particle of silica can be formed. This particle consists of an irregular 3-D network of SiO_4 tetrahedra, each silicon atom being linked to 4 oxygen atoms and each oxygen to two silicon atoms. Thus some of the silicon atoms on which the condensation reaction has not taken place or has only partially taken place will carry

1, 2 or 3 OH groups, which are still capable of further condensation. According to Carman [11], in dilute solution, the condensation results only in the increase of particle size, but in more concentrated ones ($\sim$ 1% silica), the primary particles can condense together to give a very open but continuous structure extending throughout the medium thus giving it a certain degree of rigidity - ie. gelation of the colloidal solution can occur. Upon drying of this hydrogel, the water molecules which are trapped within the gel framework will be removed and shrinkage of the gel [12] will occur to form a xerogel. During the process, the condensation reaction still continues. The particles in the hydrogel retain their individuality on drying and the pores in the xerogels are formed by interstices between contacting particles [13,14]. The final porous texture of the xerogel will depend on the conditions of preparation eg. pH, SiO_2 concentration, method of drying etc.

The surface silicon atoms can possibly carry 1, 2 or 3 OH groups - this is sometimes referred to as chemisorbed or bound water. In addition to this, molecular water may also be adsorbed on the silica surface and this is referred to as physisorbed water. Various possibilities of the arrangements of the OH groups are as indicated in Fig. 1-2.

Thus the first problem to overcome in order to study the structure of the silica surface is to distinguish between the chemisorbed and physisorbed water. One obvious way of differentiating

between the two is by heating at various temperatures, where the physisorbed water being less strongly bound is expected to be driven off at a lower temperature. There is still considerable controversy as to what temperature is needed before all the physisorbed water can be driven off without at the same time losing some of the surface hydroxyl groups (chemisorbed water). According to de Boer and Vleeskens [15,16], at 120 ^{o}C all physisorbed water will be removed and all the surface hydroxyls will still be intact while Lange [17] contends that strongly physisorbed water (eg. in narrow micropores) requires temperature of 180 ^{o}C for removal. However, at 180 ^{o}C, Young and Bursh [18] deduced that some chemically bound water has been lost.

Infrared studies have been used to try and distinguish between the two types of water. Some earlier workers have tried to use the IR absorption bands of surface silanols (at 3750 cm^{-1}, 3650 cm^{-1}, 3500 cm^{-1} and 1640 cm^{-1}) to try and resolve this problem [8]. This has led to a great deal of confusion since no real agreement has been reached in the literature as to what type of absorptions give rise to these bands. In view of this, acting on the suggestion of Wirzing [19], Erkelens and Linsen [20] used the combination band of water in the near IR region at 5625 cm^{-1} for the quantitative determination of physisorbed water and stated that this method (Wirzing's method) is best suited for distinguishing between chemisorbed and physisorbed water. They concluded that for

xerogels especially, drying at 120 ^{o}C is more or less sufficient for removing physisorbed water on the basis of reasonably good agreement between the results obtained by Wirzing's method and by the simple ignition method of de Boer and Vleeskens. It must be mentioned here however that with Wirzing's method as with all the other ignition methods, no conclusions may be drawn as to what proportions of hydroxyl groups are present on the surface and in the bulk of the silica.

Various methods have been proposed for estimating the true surface silanols from those occurring in the bulk of the particle, such as reactions with diborane, organometallic reagents, diazomethane, boron trichloride, chlorosilanes and D_2O exchange. Of these, the work of Fripiat with organometallic compounds appears to have been most successful. His results agree well with those of Kiselev who combined IR and isotopic exchange methods [21]. They showed that the OH groups in silica are located partly on the surface and partly within the elementary particles. The ratio between the quantities of surface and bulk OH groups depends on the past history of the sample and on the size of the elementary particles.

Okkerse [8] has stated that in a fully hydrated silica surface, one OH group is probably always attracted to one surface silicon atom and it is doubtful whether surface groups like $Si(OH)_2$ and $Si(OH)_3$ occur at all.

1-4 Effect of Adsorbed Cations On The Silica Gel.

Commercial silica gel is usually prepared by the neutralisation of sodium silicate with a variety of reagents eg. mineral acids, acid salts etc. Thus commercial grade silica gel usually contains ions like Na^{+}, K^{+}, Ca^{2+} etc., as impurities. The adsorption of these cations is generally attributed to the presence of hydroxyl groups which are residues from the poly-condensation of the silicic acid localized on the surface of the silica gel. For eg., the adsorption of sodium can be represented by the reaction:-

$$- Si - OH + NaOH \longrightarrow - Si - ONa + H_2O$$

However, the adsorbed cations may also be trapped within the framework of the gel, during the gelling process in which case the ions are in the bulk of the gel itself. Whether this actually occurs or not is still not certain.

Imelik and co-workers [22] have studied the adsorption of cations Ca^{2+}, Na^{+}, K^{+} and Fe^{3+} on silica gel and their effects on the porous texture of the gel. They found that K^{+} tends to decrease the specific surface of the gel and increase the size of the pores at the expense of the smaller pores. Ca^{2+} gives similar results to K^{+}. Na^{+} also tends to decrease surface area but unlike K^{+} it causes the pore distribution to become more uniform. Fe^{3+} was found to have no effect on the surface area and produced very little change in

texture. All the results quoted here refer to the data obtained by measuring the nitrogen isotherms on the gels after activating at 150 ^{o}C under vacuum, so as to study the effect of the ions on the gels. If the gel is treated differently eg. by heating at a higher temperature under atmospheric pressure, then the effect of the ions on the gel may be different from that mentioned here. They also inferred that the conditions of the treatment adopted for eliminating the free water have a great influence both on the degree of sintering and on the fine structure of the solid. If one works at atmospheric pressure, then other things being equal, the changes in texture are very much more severe.

Although from their experiments, they were not able to put forward a satisfactory explanation of the influence of the cations on the gels, they seemed to favour the idea that following thermal treatment at 150 ^{o}C, cations adsorbed on the surface hydroxyl groups enter into the actual silica gel lattice, giving rise to a structure similar to that, for example, of an alkali glass. This would mean that a certain number of Si - O - Si bridges must have been broken to enable the adsorbed cations to enter the lattice of the silica.

It might be worthwhile to note that in their experiments, the adsorbed cations are introduced into the gel itself by soaking the gel with the solutions of the cations. Thus the conclusions and observations drawn may not necessarily be the same, when a commercial

grade gel (originally containing adsorbed ionic impurities) is treated with acid and purified.

Commercial silica gels usually contain alkaline earth oxides, particularly calcia and magnesia and tervalent metal oxides especially alumina as impurities. The presence of the latter in silica will lead to the formation of strongly acidic surface sites and hence there will be an increase in the adsorptions of electron donating molecules. Thus greater heats of adsorption are to be expected for the impure gel than for the pure gel [23], and this has been found to be true for the adsorption of benzene and amines on silicas and silica-aluminas [24,25]. However, according to Iler [26], the adsorption of cations would result in the electron distribution of the adsorbed cation being shifted in such a way as to make the ion act as if it were in a lower oxidation state. Thus this polarisation of the metal ion would mean that the energy of the impure silica surface would be lowered as compared with the pure silica surface which has no such ions.

Okkerse [8] has also studied the effect of immersion in various aqueous electrolyte solutions (at 80 ^{o}C) on the texture of the silica gel. He found that in all cases the surface area decreases while the pore volume and mean pore radius remains nearly constant. He found that an aqueous immersion liquid appears to be an essential condition for the occurrence of the modification and that salt and acid solutions appear to be more effective than pure water. Also, silicas with high surface areas change more rapidly than silicas with

lower surface areas. Their distribution curves show that larger pores tend to increase while smaller pores tend to disappear. Okkerse attempted to explain his results by saying that since silica is a thermodynamically labile system, its surface area tends to decrease in an aqueous medium in which there is a dissolution of silica from the surface and a recondensation of the silica in solution with the OH groups on the surface of the solid. In this way, larger elementary particles can grow at the expense of smaller ones.

1-5 Ageing of Silica Gel.

Due to its high surface area, silica gel has a high surface energy and hence it is thermodynamically not stable. Accordingly, it will tend to lose its activity as soon as it is formed by the process of ageing which almost always results in a decrease in surface area amongst other things. Ageing can occur just merely by storing the gel over a period of time, though under ordinary conditions it is usually very slow (however some extreme cases in which active titania stored for about 2 weeks at 50 ^{o}C have had their surface areas decreased by over 50% have been known [27]).

The process and mechanism of ageing and sintering (which is the adhesion of the particles of a solid to form aggregation at elevated temperatures) of silica gels and silica-alumina cracking catalyst in the presence of steam and high temperatures have been studied rather extensively [28-31]. Ries [28] found that during ageing

at high temperatures (800 - 1000 ^{o}C) in high vacuum, the distribution of pore radii (as defined by the Kelvin equation) remains almost unchanged and the average pore radius (as defined by $\frac{2 \times \text{Pore Volume}}{\text{Surface Area}}$) remains approximately constant. However at lower temperatures (500 - 600 ^{o}C) in the presence of steam, the average pore radius increases considerably, the distribution of pore radii broadens and the median pore radius increases. Schlaffer et al [29,31] extended the work of Ries on the ageing of silica-alumina catalyst and silica gels and proposed a model and possible mechanisms whereby the loss in surface area and pore volume can be accounted for. They proposed a model in which the catalysts and gels are thought to consist of small impervious particles bonded together by bridges of the same material. The surface of the particles give rise to the surface area and the interstitial space among the particles is the pore volume.

The processes by which they postulate the ageing to occur are (i) growth of large particles at the expense of smaller ones by a surface process such as vapour phase transport, (ii) a process which results in the fusion of large number of ultimate particles with the possible entrapment of voids, (iii) a collapse of the aggregate structure as a result of stresses set up by, (i) and (ii). From their results, they also concluded that the difference between ageing of silica and silica-alumina is that processes (ii) and (iii) are relatively more important for the silica gel.

As mentioned earlier, Okkerse [8] investigated the effect on the texture of silica xerogel when it is soaked in various solutions and liquids at 80 ^{o}C and he found that there was a strong similarity between his results and the results of Schlaffer et al on the effect of steam treatment at 500 ^{o}C on cracking catalysts. From this, he suggested that the mechanisms of the two effects are probably the same.

CHAPTER 2 INTRODUCTION TO ADSORPTION STUDIES

2-1 Theories of Adsorption

One of the earliest theories of adsorption which has had some success is the Polanyi potential theory. This theory has been discussed in detail by Brunauer [32] and in its simplest form assumes that the forces holding a molecule to the surface decay exponentially with distance. The force of attraction at any given point in the adsorbed film is measured by the adsorption potential, E, and E decreases from its maximum value E_o at the adsorbent surface to zero at the outermost layer where the density is equal to that of the surrounding gas. The process of building up the adsorbed film is represented by the distribution function $E = f(\phi)$ where ϕ is the volume of adsorption space. The Polanyi theory is of limited use because it does not give an isotherm equation relating pressure and amount adsorbed and it provides very little information about the structure or the thickness of the adsorbed film. Nevertheless, it is successful in predicting the temperature dependence of physical adsorption [33,34]. Dubinin [35] and his collaborators have modified the Polanyi theory and have derived an expression for the adsorption isotherms which was found to be applicable at low relative pressures (from 1×10^{-5} to 0.2) to microporous solids +. However adequate confirmation of

+ Pores have been divided into 3 types according to their sizes [36]. Pores of widths below about 20 Å are described as micropores, those with widths above about 500 Å are termed macropores while those pores of intermediate widths are referred to as mesopores.

the Dubinin method is still lacking [37].

Unlike Polanyi, Langmuir [38] focused attention on the process of interchange of molecules between the gas phase and the adsorbed film thereby adopting a kinetic approach to the problem. He treated adsorption as the formation of a single or monomolecular layer and visualised adsorption as a kinetic process in which molecules collide with the solid surface and after a short time lag they evaporate. In his theory he assumed that the adsorption is localised, the heat of adsorption for every molecule is the same and any molecule striking any other molecule already adsorbed returns immediately to the gas phase. Langmuir was able to derive an equation which was able to predict the isotherm shape for some systems but it proved to be unsatisfactory for many systems. In 1938, Brunauer, Emmett and Teller [39] following the path laid down by Langmuir produced a theory (the so-called BET theory) which accounts fairly well for the majority of isotherms that have been observed. Their theory retains the concept of fixed adsorption sites proposed by Langmuir, but allows for the formation of adsorbed layers which are more than one molecule thick. The state of dynamic equilibrium which Langmuir postulated for monomolecular layer is assumed to hold in the BET theory for each successive molecular layer. Furthermore it is also assumed that the heat of adsorption in each layer other than the first is equal to the heat of liquefaction of the bulk adsorbate material.

The BET isotherm equation for a free surface (where it is assumed that an infinite number of layers may be adsorbed) is given by

$$\frac{P}{V(P_o-P)} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P_o} \qquad (2\text{-}1)$$

where V is the total volume adsorbed at the measured pressure P, V_m is the volume adsorbed as a monolayer; P_o is the saturation vapour pressure of the adsorbate and c is a constant that is related exponentially to the heat of adsorption and the heat of liquefaction of the adsorbate. The BET equation is obeyed if the plot of $\frac{P}{V(P_o-P)}$ versus P/P_o is a straight line and from the slope and intercept, V_m and c can be found. It has been found that equation (2-1) reproduces the course of many isotherms reasonably well particularly over the range $0.05 < P/P_o < 0.35$. However, there are many instances where the range of linearity of equation (2-1) does not extend to relative pressures as high as 0.30 or 0.35 [40,41].

If for some reasons (eg. small diameters of pore walls) the number of layers is limited to the finite number, n, even at saturation, the BET treatment leads to the modified equation

$$\frac{V}{V_m} = \frac{cP/P_o}{1-P/P_o}\left[\frac{1-(n+1)(P/P_o)^n + n(P/P_o)^{n+1}}{1+(c-1)P/P_o - c(P/P_o)^{n+1}}\right] \qquad (2\text{-}2)$$

Equation (2-2) may be regarded as a general equation which includes as a special case the standard BET equation (equation (2-1)) by

putting $n = \infty$ and also the Langmuir equation by putting $n = 1$. A fuller treatment of restricted adsorption has been given by Brunauer et al. [42], but the resulting equation is so complicated that it is rarely used in practice.

Several defects in the BET theory have been pointed out by a number of workers [43-47]. In spite of its theoretical short-comings it is still widely used to determine specific surface areas. A number of modifications to the BET theory have been suggested [48-54]. These usually enable the equation to fit a wider range but generally involve the introduction of an arbitrary extra parameter. Thus the better agreement between calculated and observed isotherms may be due solely to the added flexibility conferred on the equation by the new parameter.

Huttig [55] has derived an adsorption equation using assumptions which are similar to the BET theory except for the fact that he assumes that evaporation from the second and higher layers occur as freely as if the higher layers are not present. Although the Huttig equation has been shown to be thermodynamically unsound [56], it has been applied as an empirical equation.

An approach quite different from the kinetic theories of the BET and Langmuir, but resembling the point of view of Polanyi's potential theory, has been adopted by Frenkel, Halsey and Hill [57-59]. Independently they developed what is now known as the 'Slab Theory' of multimolecular adsorption which can be applied to

adsorption greater than 2 layers. They considered the problem of restricted adsorption of a spherically symmetrical molecule on a nonporous, nonpolar adsorbent for $V/V_m > 2$. As far as molecules being adsorbed in the third and higher layers are concerned, the effects of the detailed structure of the adsorbent surface are effectively smoothed out and the molecular environment of these molecules is not very different from that of the corresponding molecules in the bulk liquid. The remaining effect which is predominant in determining the adsorption behaviour is the potential energy field in which a molecule is adsorbed compared with the field in the bulk liquid. The equation they obtained can be written as,

$$\ln(P/P_o) = \frac{-k}{(V/V_m)^a} \qquad (2\text{-}3)$$

where k and a are constants. In their derivations they found that a = 3 but in actual systems, a is found not equal to 3.

Attempts to interpret the adsorption isotherm from a thermodynamic standpoint have also been made and one of the most important of these is that of Harkins and Jura [60]. They suggested that the equation describing the behaviour of a film on water at high surface pressure given by

$$\pi = b - qA \qquad (2\text{-}4)$$

where π = the surface pressure of adsorbed film

A = molecular area of the film

b, q = constants

may also hold for a film of gas adsorbed on a solid. From (2-4) the Harkins-Jura equation,

$$\ln(P/P_o) = D - C/x^2 \qquad (2\text{-}5)$$

where x is the weight of gas adsorbed at pressure P and D, C are constants, may be derived [61].

Thus according to equation (2-5), a plot of $\ln(P/P_o)$ versus $1/x^2$ should give a straight line of slope C, where the constant C is given by the equation,

$$C = \frac{qM^2S^2}{2NRT} \qquad (2\text{-}6)$$

where M = molecular wt. of adsorbate

S = surface area of adsorbent

N = Avogadro's number

R = gas constant

T = absolute temperature

The surface area, S, can be calculated provided q is known. Harkins and Jura assumed that q remains constant for a given vapour on different adsorbents (similar to the constancy of q for films of a given fatty acid on water when the pH is varied) and thus were able to assign a value of q to each vapour at a given temperature if once an isotherm of that vapour has been measured on a single adsorbent of known area. Gregg and Sing [62] have discussed about the reliability of the Harkins-Jura method of surface area determination and are of the opinion that the BET method is preferable. One major weakness of the Harkins-Jura

method is that in drawing analogy with films of water the effect of the heterogeneity of the solid surface is ignored.

Another theory of adsorption which has been proposed is the capillary condensation theory. It has long been known that for a liquid that wets the wall of a capillary, its vapour pressure in the capillary will be lower than in the normal bulk phase. Assuming this to be still true when the size of the capillaries are in the order of the pores that are present in adsorbents, Zsigmondy [63], put forward the idea that in such adsorbents the adsorbate can condense in the capillaries at pressures far below the normal vapour pressure. To-day practically all investigators of adsorption phenomena agree that capillary condensation plays some role in physical adsorption but there is still no general agreement as to how great a role is to be assigned to it. Brunauer [64] has discussed in great length the capillary condensation theory of physical adsorption and he summarised it up by saying that the theory cannot account for adsorption at low pressure, but at higher pressure it probably plays an important role for all adsorbents except those that have exceedingly fine pores.

2-2 Hysteresis

In general, the isotherms of most porous adsorbents show hysteresis. Several hypotheses have been put forward to account for this behaviour, and the most satisfactory ones are all based on

the capillary condensation theory. It has been mentioned before, that in capillaries, condensation of the gas or vapour can take place even when the pressure is below the saturation vapour pressure and the general expression describing this can be written in the form [65]

$$\frac{dv}{dS} = - \frac{V_L \gamma \cos \phi}{RT \ln(P/P_o)} \qquad (2\text{-}7)$$

where v is the volume of the capillaries, S the surface area of their walls per gram of solid, V_L is the molar volume of the condensed adsorbate, γ the surface tension, and ϕ is the angle of contact between the condensed liquid and the walls of the capillary, P_o is the saturation vapour pressure of the adsorbate.

If the capillaries or pores are circular in cross-section (or cylindrically shaped), then equation (2-7) reduces to the form,

$$r_k = \frac{- 2V_L \gamma \cos \phi}{RT \ln(P/P_o)} \qquad (2\text{-}8)$$

where r_k is the radius of the capillary. Henceforth the r_k as calculated from (2-8) will be referred to as the Kelvin radius. Equation (2-8) is also known as the Kelvin equation. In the following discussion on the role of capillary condensation in hysteresis phenomenon, it will be assumed for simplicity that the Kelvin equation can be applied. In actual cases this may not be so, but provided the pore system is not too complex the relationship between the Kelvin radius and the parameter or parameters which

describe the pores can be worked out [66].

A) Theories of Hysteresis

At first it was thought that hysteresis was due to the presence of traces of air during adsorption [63] so that the contact angle of the liquid adsorbate (given by the Kelvin equation) in the pores is greater than zero whereas during desorption, all the pores having been filled and completely wetted, has a contact angle of zero. So for a given r_k (i.e. a given amount sorbed), P/P_o for capillary condensation during adsorption will be greater than P/P_o for capillary evaporation during desorption. However, this hypothesis was soon proven to be untrue, for isotherms in which air has been carefully excluded still showed hysteresis [67].

Cohan [68] and Coelingh [69] independently proposed that hysteresis in open-ended cylindrical pores can be explained by the shape of the meniscus during adsorption and desorption. For adsorption the meniscus is cylindrically shaped, hence capillary condensation will occur at $r_k = 2r$ (where r = radius of capillary) but for desorption the meniscus is now spherically shaped and capillary evaporation will occur at $r_k = r$. So, for a given amount adsorbed,

$$(P_a/P_o)^2 = P_d/P_o \qquad (2\text{-}9)$$

where P_a, P_d are the pressures on the adsorption and desorption branches respectively.

One obvious drawback of this hypothesis is that truly

cylindrical pore systems even those with differing pore radii are hard to find in practice. One would expect that actual pore systems would more likely consist of capillaries of unequal dimensions along its length; i.e. capillaries with constrictions. This leads to yet another explanation of hysteresis phenomenon put forward by McBain [70] and others [67,71]. They envisaged capillaries having constrictions at one end and the other end being closed, and so they are shaped like 'ink-bottles' or 'erlenmeyer flasks'. For such capillaries, during adsorption, capillary condensation will occur at $r_k = r_w$ (see Fig. 2-1). For desorption since the cavity is now full, at

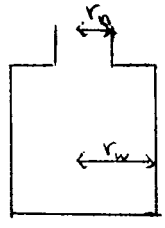

Fig. 2-1 An 'ink-bottle' pore

a pressure corresponding to r_w, it will not desorb, rather it is the radius of the narrow neck r_n, that determines at which pressure evaporation takes place. Since $r_n < r_w$, it follows that the pressures at which the capillary fills and empties are not equal, resulting in hysteresis.

Foster [72] put forward the hypothesis that in open pores (pores open on both sides e.g. slit shaped pores formed by parallel platelets) hysteresis is due to a delay in the formation of the meniscus during the adsorption process i.e. along the adsorption branch, capillary condensation cannot take place even though the

Kelvin radius, has been reached. Thus there is only multilayer build-up of adsorbate until the adsorbed multilayer is thick enough to block the narrowest part of the pore when capillary condensation occurs immediately in the pore. At saturation however, all the pores have been filled, and menisci is present in every pore, hence the Kelvin equation can be obeyed for capillary evaporation during desorption. Foster's hypothesis can probably explain hysteresis in slit-shaped pores but for other types of pores some evidence has been found against it [73].

An alternative approach to the mechanism of condensation and evaporation in capillaries has been proposed by Everett and Haynes [74,75]. This mechanism unlike the others discussed so far, takes into account the mechanical or Laplace stability of the condensed liquid in addition to the usual consideration of stability with respect to the vapour pressure or Kelvin stability. Using the model of a uniform cylindrical capillary, they showed that during the process of condensation and evaporation the liquid/vapour interface passes through a series of intermediate states having the form of unduloidal surfaces (surfaces of constant curvature). The formation of unduloids in capillary condensation is caused by Laplace instability where the cylindrical film is unstable with respect to changes in shape. The changes which take place in the cylindrical capillary during condensation and evaporation, according to the theory of Everett and Haynes, are illustrated in the figures

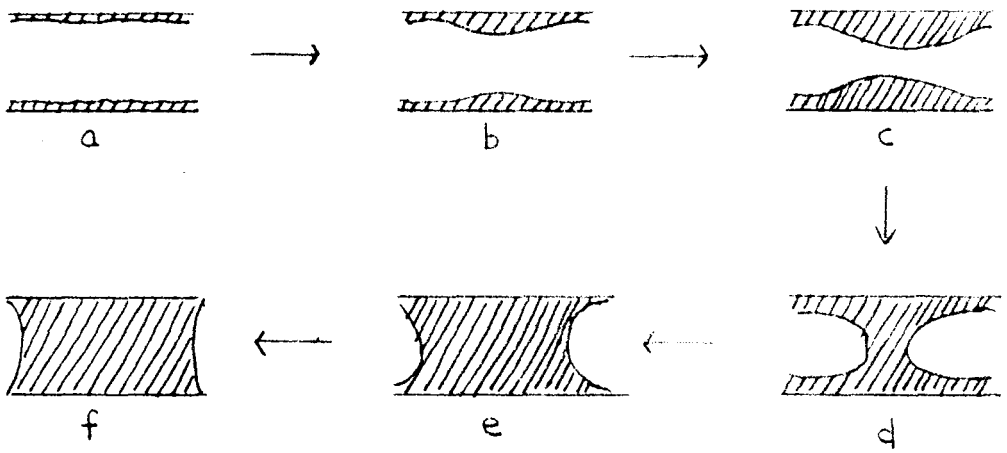

FIG. 2-2 CONDENSATION IN A CYLINDRICAL CAPILLARY.

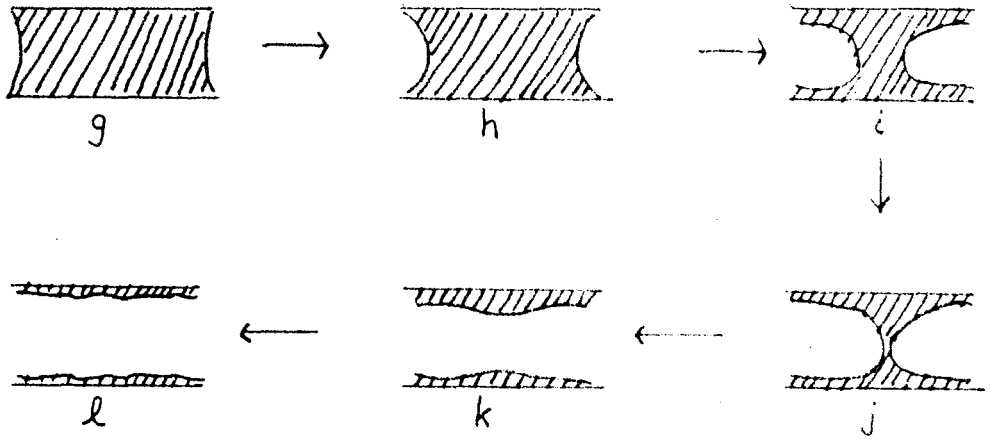

FIG. 2-3 EVAPORATION IN A CYLINDRICAL CAPILLARY.

(2-2) and (2-3). When the capillary is sufficiently long, i.e. the length $\gg$ the circumference, the cylindrical film formed in state (a) (Fig. 2-2) is Laplace unstable and changes to an unduloid (b), which is Laplace stable but Kelvin unstable. With increasing pressure, the unduloid grows in volume, (c), until it becomes Laplace unstable and the system transforms spontaneously to state (d), where a biconcave lens is formed. Further increase in the volume of liquid in the capillary occurs reversibly at constant curvature by increase in the length of the thread of liquid, (e), and in this way the whole capillary is filled, (f). The transition from an unduloid to a lens bounded by hemispherical menisci will not take place at the point where the two configurations have the same effective area because the route between them at constant volume involves passage over an effective area barrier which is essentially a free energy barrier. The transition is delayed until state (c) is reached when the barrier disappears and a spontaneous rearrangement of the system occurs with a reduction in effective area and dissipation of free energy. Similarly during evaporation, the emptying occurs reversibly until the retreating menisci meet 'back to back' (Fig. 2-3 (j)), and the film between them bursts irreversibly with a reduction in effective area. Thus the theory of Everett and Haynes demonstrates that spontaneous processes occur during both condensation and evaporation and for hysteresis arising from capillary condensation in an assembly of capillaries, neither branch of the hysteresis loop is reversible.